



(11) **EP 1 749 322 B1**

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention of the grant of the patent:
31.12.2008 Bulletin 2009/01

(51) Int Cl.:
H01M 4/92^(2006.01) H01M 8/10^(2006.01)
B01J 23/42^(2006.01) C22C 5/04^(2006.01)

(21) Application number: **05744788.0**

(86) International application number:
PCT/GB2005/001918

(22) Date of filing: **19.05.2005**

(87) International publication number:
WO 2005/117172 (08.12.2005 Gazette 2005/49)

(54) **ANODE STRUCTURE FOR FUEL CELL**
ANODENSTRUKTUR FÜR EINE BRENNSTOFFZELLE
STRUCTURE D'ANODE POUR PILE A COMBUSTIBLE

(84) Designated Contracting States:
DE ES FR GB IT NL

(30) Priority: **26.05.2004 GB 0411733**

(43) Date of publication of application:
07.02.2007 Bulletin 2007/06

(73) Proprietor: **Johnson Matthey Public Limited Company**
London EC1N 8EE (GB)

(72) Inventors:
• **BALL, Sarah, Caroline**
Oxon OX10 9NX (GB)
• **THOMPSETT, David**
Reading RG4 7BQ (GB)

(74) Representative: **Nunn, Andrew Dominic et al**
Johnson Matthey Technology Centre,
Blount's Court,
Sonning Common
Reading,
Berkshire RG4 9NH (GB)

(56) References cited:
EP-A- 0 736 921 EP-A- 0 838 872
EP-A- 0 899 805 WO-A-00/35037
WO-A-02/091504 WO-A-20/04091004
US-A- 5 871 860

- **GÖTZ M. ET AL.:** "Binary and ternary anode catalyst formulations including the elements W, Sn and Mo for PEMFCs operated on methanol or reformat gas" **ELECTROCHIMICA ACTA**, vol. 43, no. 24, 21 August 1998 (1998-08-21), pages 3637-3644, XP004132402 ISSN: 0013-4686
- **GRGUR B.N. ET AL.:** "Electrooxidation of H₂/CO mixtures on a Well-characterized Pt₂₅Mo₂₅ Alloy surface" **JOURNAL OF PHYSICAL CHEMISTRY B**, vol. 101, no. 20, 1997, pages 3910-3913, XP002112464 ISSN: 1089-5647

EP 1 749 322 B1

Note: Within nine months of the publication of the mention of the grant of the European patent in the European Patent Bulletin, any person may give notice to the European Patent Office of opposition to that patent, in accordance with the Implementing Regulations. Notice of opposition shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

Description

[0001] The present invention relates to an anode structure for incorporation in a fuel cell, particularly a fuel cell that is fuelled by reformat gas comprising carbon monoxide.

[0002] A fuel cell is an electrochemical cell comprising two electrodes separated by an electrolyte. A fuel, e.g. hydrogen or methanol, is supplied to the anode and an oxidant, e.g. oxygen or air, is supplied to the cathode. Electrochemical reactions occur at the electrodes, and the chemical energy of the fuel and the oxidant is converted to electrical energy and heat. Fuel cells are a clean and efficient power source, and may replace traditional power sources such as the internal combustion engine in both stationary and automotive power applications.

[0003] In a polymer electrolyte membrane (PEM) fuel cell, the electrolyte is a solid polymer membrane which is electronically insulating but ionically-conducting. Proton-conducting membranes such as those based on perfluorosulphonic acid materials are typically used, and protons, produced at the anode, are transported across the membrane to the cathode, where they combine with oxygen to create water.

[0004] The principle component of a polymer electrolyte fuel cell is known as a membrane electrode assembly (MEA) and is essentially composed of five layers. The central layer is the polymer membrane. On either side of the membrane there is an electrocatalyst layer, typically comprising a platinum-based electrocatalyst. An electrocatalyst is a catalyst that promotes the rate of an electrochemical reaction. Finally, adjacent to each electrocatalyst layer there is a gas diffusion substrate. The gas diffusion substrate must allow the reactants to reach the electrocatalyst layer and must conduct the electric current that is generated by the electrochemical reactions. Therefore the substrate must be porous and electrically conducting.

[0005] In many practical fuel cell systems hydrogen fuel is produced by converting a hydrocarbon fuel (such as methane or gasoline) or an oxygenated hydrocarbon fuel (such as methanol) to a gas stream known as reformat in a process known as reforming. The reformat gas contains hydrogen, about 25% carbon dioxide, small amounts of carbon monoxide (typically at levels of around 1%) and may contain other contaminants. For fuel cell operating temperatures below 200°C and especially for PEM fuel cells operating at temperatures of around 100°C, carbon monoxide, even at levels of 1-10ppm, is a severe poison for the platinum electrocatalyst in the anodes of the MEAs. This leads to a significant reduction in fuel cell performance (i.e. the cell voltage at a given current density is reduced).

[0006] To alleviate anode carbon monoxide poisoning, most reformer systems include an additional catalytic reactor known as a preferential or selective oxidation reactor. Air or oxygen is injected into the reformat gas stream, which is then passed over a selective oxidation catalyst which oxidises the carbon monoxide to carbon dioxide. This can reduce the levels of CO from about 1% down to below 100ppm, but even at these levels the anode electrocatalyst is poisoned.

[0007] WO 00/35037 discloses carbon monoxide tolerant anodes comprising a first electrocatalyst of formula Pt-Y, wherein Y is a bronze forming element, and a second electrocatalyst of formula Pt-M, wherein M is a metal alloyed with the platinum, wherein the first and second electrocatalysts are in ionic contact. The first and second electrocatalysts may be formulated into two separate layers, which are applied to the one side of the gas diffusion substrate or to the membrane. Alternatively, the first and second electrocatalysts may be mixed together and formed into one layer containing both catalysts. Membrane electrode assemblies comprising the anodes exhibit good performance even at levels of 100ppm CO.

[0008] WO 2004/091004 discloses a membrane-electrode assembly comprising an ionically-conductive proton exchange membrane with a major surface and an electrode disposed at said major surface, said electrode comprising: a first group of catalytic particles which catalyse oxidation of carbon monoxide to carbon dioxide and which catalyse an electrochemical reaction releasing protonic (H⁺) species when in contact with ionically-conductive material; and a second group of catalytic particles which catalyse an electrochemical reaction releasing electrons; where said first and second group of particles are different.

[0009] US 5,871,860 discloses a gas-liquid permeable porous electrode comprising one or more electrode layers supported on one side of a substrate, wherein at least one of the one or more electrode layers comprises an electrocatalyst material, wherein the electrode layer comprising the electrocatalyst material comprises a first region adapted to be adjacent a bulk gas inlet and wherein said first region has a first amount of the electrocatalyst material, and a second region, at a point remote from the first region, said second region having a second amount of the electrocatalyst material, said second amount being different from the first.

[0010] EP 0 736 921 discloses an electrode comprising a first catalytic component active at gas phase reaction sites and a second catalytic component active at electrochemical reaction sites wherein each catalytic component is present either as a separate layer, or a single mixed layer or a combination of a separate layer and a single mixed layer. The electrode has an improved tolerance to poisons such as carbon monoxide and carbon dioxide.

[0011] WO 02/091504 discloses a PEM fuel cell having an anode backing formed of a porous electrically conductive material and having a first surface abutting the electrocatalytic surface and a second surface facing away from the membrane, where the second surface has an oxidation catalyst layer effective to catalyse the oxidation of CO by oxygen present in the fuel stream.

[0012] EP 0 899 805 discloses a CO-tolerant electrode suitable for use in a fuel cell formed from a carbon supported, platinum dispersed, non-stoichiometric hydrogen tungsten bronze electrode catalyst.

[0013] EP 0 838 872 discloses a novel catalyst comprising a Pt-M alloy wherein M is one or more metals selected from the transition metal elements of from Groups IIIA or IVA of the Periodic Table and Y wherein Y is a bronze forming element or an oxide thereof, and wherein Pt-M alloy is in intimate contact with Y.

[0014] Electrochimica Acta, vol. 43, no. 24, pp 3637-3644 discloses binary and ternary carbon supported catalysts with the elements Pt and Ru, W, Mo or Sn and which were tested for their activity for anodic oxidation of H₂ containing 150ppm CO and of methanol.

[0015] J. Phys. Chem. B, vol. 101, no. 20, pp 3910-3913 discloses the examination of the electrochemical oxidation of hydrogen in the presence of carbon monoxide (0.05-2%) on a well-characterised Pt₇₅Mo₂₅ alloy surface.

[0016] The present inventors have sought to provide anode structures that are tolerant to even higher levels of carbon monoxide and/or carbon dioxide, or that have similar carbon monoxide tolerance at lower electrocatalyst loadings.

[0017] Accordingly, the present invention provides an anode structure for incorporation into a fuel cell comprising a fuel inlet and a fuel outlet, wherein the anode structure comprises:

a first region comprising an electrocatalyst of formula Pt-Y or Pt-Y-X, wherein Y is a bronze-forming element or Sn, or an oxide thereof, and X is one or more metals alloyed with the platinum, wherein the first region will be adjacent to the fuel inlet when the anode structure is incorporated into a fuel cell;

a second region comprising an electrocatalyst for the electrochemical oxidation of hydrogen of formula Pt-M, wherein M is a metal alloyed with the platinum and is selected from the group consisting of Ru, Rh, Ti, Cr, Mn, Fe, Co, Ni, Cu, V, Ga, Zr and Hf, wherein the second region will be adjacent to the fuel outlet when the anode structure is incorporated into a fuel cell;

wherein the first region is better at promoting the electrochemical oxidation of carbon monoxide than the second region.

[0018] Reformate gas comprising carbon monoxide that is supplied to a fuel cell comprising the anode structure will contact the first region of the anode structure before it reaches the second region. The electrochemical oxidation of carbon monoxide is promoted by the first region, so the gas reaching the second region will have a reduced concentration of carbon monoxide:



The electrochemical reaction is promoted by the electrocatalyst in the first region, which must be in ionic contact with the proton-conducting membrane. The electrocatalysts in the first region can be optimised for carbon monoxide removal, whilst the electrocatalysts in the second region do not need to have high tolerance to carbon monoxide. By tailoring the electrocatalysts in this manner, an overall lower loading of platinum on the anode can be achieved. Additionally, the anode structure can tolerate higher levels of carbon monoxide (up to 1000ppm).

[0019] The term "anode structure" for the purposes of the present description means the parts of an electrochemical cell wherein the anodic electrochemical reactions take place. The physical embodiments of the "anode structure" can take several forms. The anode structure may comprise electrocatalysts applied to one face of a gas diffusion substrate. Alternatively, the anode structure may comprise electrocatalysts applied to one face of a polymer electrolyte membrane.

[0020] Suitably the first region covers between 5-50% of the surface area of the anode structure, and the second region covers the remainder of the surface area. The shape and size of the first region will be dependent on the flow field design. The incoming gas will contact the first region before contacting the second region.

[0021] Suitably the first region comprises an electrocatalyst of formula Pt-Y or Pt-Y-X, wherein Y is a bronze-forming element or oxide thereof or Y is Sn, and X is one or more metals alloyed with the platinum. Component Y may be alloyed with the Pt or the Pt-X alloy, or may be unalloyed but in physical contact with the alloy. A "bronze" material is defined by Wold and Dwight in 'Solid State Chemistry - Synthesis, Structure and Properties of Selected Oxides and Sulfides' as "an oxide with intense colour (or black), having a metallic lustre and showing either semi-conducting or metallic behaviour. A principle characteristic of bronzes is their range of composition, which results in the transition metal exhibiting a variable formal valence". Y is suitably selected from the group consisting of Sn, Ti, V, Nb, Ta, Mo, W, Re or an oxide thereof; preferably from Sn, Ti, V, Ta, Mo, W or an oxide thereof; most preferably from Sn, Mo or W or an oxide thereof. X is suitably one or more metals selected from the group consisting of Ru, Rh, Ti, Cr, Mn, Fe, Co, Ni, Cu, V, Ga, Zr and Hf and is preferably one or more of Ru, Mn, Ti, Co, Ni and Rh. A preferred electrocatalyst for the first region is Pt-Mo.

[0022] In a particular embodiment of the invention, the first region further comprises an electrocatalyst for the electrochemical oxidation of hydrogen and the electrocatalyst is preferably of formula Pt-M, wherein M is a metal alloyed with the platinum and is selected from the group consisting of Ru, Rh, Ti, Cr, Mn, Fe, Co, Ni, Cu, V, Ga, Zr and Hf.

[0023] In an alternative embodiment of the invention, the first region does not contain any electrocatalysts other than the electrocatalyst of formula Pt-Y or Pt-Y-X, wherein Y is a bronze-forming element or oxide thereof and X is one or

more metals alloyed with the platinum. This is preferred because the electrocatalyst in the first region can be optimised for the oxidation of carbon monoxide.

[0024] Suitably the second region comprises an electrocatalyst for the electrochemical oxidation of hydrogen and preferably the electrocatalyst is of formula Pt-M, wherein M is a metal alloyed with the platinum and is selected from the group consisting of Ru, Rh, Ti, Cr, Mn, Fe, Co, Ni, Cu, V, Ga, Zr and Hf.

[0025] In a preferred embodiment of the invention, the first region comprises only one electrocatalyst, and the electrocatalyst is of formula Pt-Y or Pt-Y-X, wherein Y is a bronze-forming element or oxide thereof and X is one or more metals alloyed with the platinum, and the second region comprises only one electrocatalyst, and the electrocatalyst is of formula Pt-M, wherein M is a metal alloyed with the platinum and is selected from the group consisting of Ru, Rh, Ti, Cr, Mn, Fe, Co, Ni, Cu, V, Ga, Zr, Hf and Sn. In a most preferred embodiment of the invention, the first region comprises only one electrocatalyst, and the electrocatalyst is Pt-Mo, and the second region comprises only one electrocatalyst, and the electrocatalyst is Pt-Ru.

[0026] To prepare an anode structure according to the invention electrocatalysts can be deposited onto a suitable substrate using any suitable techniques known to the skilled person. The electrocatalysts may be prepared using standard techniques such as those disclosed in WO 00/35037. The electrocatalysts may be finely divided metal powders (metal blacks), or may be supported catalysts wherein small metal particles are dispersed on electrically conducting particulate carbon supports. Preferably the electrocatalysts are supported catalysts.

[0027] The substrate may be a gas diffusion. Typical gas diffusion substrates are based on carbon paper (eg Toray® paper available from Toray Industries, Japan), woven carbon cloths (eg Zoltek® PWB-3 available from Zoltek Corporation, USA) or nonwoven carbon fibre webs (eg Optimat 203 available from Technical Fibre Products, UK). The carbon substrate is typically modified with a particulate material either embedded within the substrate or coated onto the planar faces, or a combination of both. The particulate material is typically a mixture of carbon black and a polymer such as polytetrafluoroethylene (PTFE).

[0028] The substrate may be a polymer electrolyte membrane. State-of-the-art membranes are often based on perfluorinated sulphonic acid materials such as Nafion® (DuPont), Flemion® (Asahi Glass) and Aciplex® (Asahi Kasei). The membrane may be a composite membrane, containing the proton-conducting material and other materials that confer properties such as mechanical strength. For example, the membrane may comprise a proton-conducting membrane and a matrix of silica fibres, as described in EP 875 524. The membrane is suitably less than 200µm thick, preferably less than 50µm thick.

[0029] Suitably the electrocatalysts are formulated into electrocatalyst inks, e.g. as disclosed in EP 731 520, before application to the substrate. The inks can be applied using technique such as screen printing or spraying. To apply the inks to only the first region or only the second region, masks may be used.

[0030] The present invention further provides a membrane electrode assembly comprising an anode structure according to the invention. The person skilled in the art can prepare membrane electrode assemblies using well-known methods. Two gas diffusion electrodes (the anode being an anode structure according to the invention) can be placed either side of a membrane and laminated together to form the five-layer MEA. Alternatively, electrocatalyst layers may be applied to both faces of a membrane to form a catalyst coated membrane (CCM), such that one of the electrocatalyst layers is an anode structure according to the invention. Subsequently, gas diffusion substrates are applied to both faces of the catalyst coated membrane.

[0031] The present invention yet further provides a fuel cell having a fuel inlet and a fuel outlet, wherein the fuel cell comprises an anode structure and the anode structure comprises a first region comprising an electrocatalyst of formula Pt-Y or Pt-Y-X, wherein Y is a bronze-forming element or Sn, or an oxide thereof, and X is one or more metals alloyed with the platinum, wherein the first region is adjacent to the fuel inlet, a second region comprising an electrocatalyst for the electrochemical oxidation of hydrogen of formula Pt-M, wherein M is a metal alloyed with the platinum and is selected from the group consisting of Ru, Rh, Ti, Cr, Mn, Fe, Co, Ni, Cu, V, Ga, Zr and Hf, wherein the second region is adjacent to the fuel outlet, wherein the first region is better at promoting the electrochemical oxidation of carbon monoxide than the second region.

[0032] The person skilled in the art can incorporate anode structures into fuel cell structures using well-known methods.

[0033] In a further aspect the present invention provides a method of using a fuel cell according to the invention wherein reformat gas is supplied to the fuel cell.

[0034] The reformat gas stream may be formed using standard reformer apparatus and is likely to comprise hydrogen, carbon dioxide, carbon monoxide and other impurities. The concentration of carbon monoxide is suitably from 10-10,000ppm, preferably from 20-5000ppm. The method of the present invention can be carried out using higher concentrations of carbon monoxide than can typically be supplied to known fuel cells.

[0035] For a more complete understanding of the invention, reference is made to the schematic drawings wherein:

Fig. 1 is a schematic diagram showing an anode structure according to a first embodiment of the invention.

Fig. 2 is a schematic diagram showing an anode structure according to a second embodiment of the invention.

Fig. 3 is a schematic diagram showing a cross-section of a fuel cell according to an embodiment of the invention.

[0036] Fig. 1 shows an anode structure (1) wherein a first electrocatalyst region (3) and a second electrocatalyst region (4) are deposited on a gas diffusion substrate (2).

[0037] Fig. 2 shows an anode structure (1) wherein a first electrocatalyst region (3) and a second electrocatalyst region (4) are deposited on a proton-conducting membrane (5).

[0038] Fig. 3 shows a cross-section of a fuel cell wherein the edge of the anode structure (1) is shown by a dashed line. Fuel is supplied to the fuel cell through fuel inlet (6) and passes along channels in the field flow plate (8). Unreacted fuel and product gases pass through the fuel outlet (7). The fuel initially contacts the first electrocatalyst region (3) and carbon monoxide in the fuel is depleted before it reaches the second electrocatalyst region (4).

[0039] The invention will now be described by reference to example which is intended to be illustrative and not limiting of the invention.

Manufacture of Membrane Electrode Assemblies

[0040] Two different catalysts were used: a platinum-ruthenium on carbon black catalyst (HiSpec® 10,000 available from Johnson Matthey plc) and a platinum-molybdenum on carbon black catalyst (20wt% Pt, 4.5wt% Mo on Vulcan® XC72-R prepared according to the methods outlined in WO 00/35037). The catalysts were formulated into catalyst inks using the methods disclosed in EP 731 520. Four anode substrates were manufactured by screen-printing the inks onto Toray® paper covered with a carbon black/PTFE base layer:

	Catalyst	Platinum Loading (mg Pt/ cm ²)
Example 1	PtMo/ PtRu	0.34
Comparative Example 1	PtRu	0.5
Comparative Example 2	PtRu	0.23
Comparative Example 3	PtMo	0.23

[0041] The anode substrate of Example 1 contained a region of PtMo catalyst and a region of PtRu catalyst. Each region covered 50% of the surface area of the catalysed area.

[0042] The anode substrates were combined with membranes and cathodes to form membrane electrode assemblies and were tested in a fuel cell. The membrane electrode assembly containing the example 1 substrate was positioned such that the PtMo half of the substrate was adjacent to the fuel cell inlet. The membrane electrode assemblies were tested with pure hydrogen, hydrogen containing 100ppm carbon monoxide and hydrogen containing 25% carbon dioxide. The performance decrease in mV for each membrane electrode assembly for the carbon monoxide and carbon dioxide containing fuels (as compared to pure hydrogen) was calculated:

	Performance loss due to 100ppm CO (mV)	Performance loss due to 25% CO ₂ (mV)
Example 1	78	30
Comparative Example 1	77	19
Comparative Example 2	126	22
Comparative Example 3	52	45

[0043] The anode substrate according to the invention (example 1) provides comparable carbon monoxide tolerance to a PtRu catalysed substrate with substantially higher platinum loading (comparative example 1). The anode substrate according to the invention provides better carbon dioxide tolerance than a PtMo catalysed substrate (comparative example 3).

Claims

1. An anode structure for incorporation into a fuel cell comprising a fuel inlet and a fuel outlet, wherein the anode structure comprises:

a first region comprising an electrocatalyst of formula Pt-Y or Pt-Y-X, wherein Y is a bronze-forming element or Sn, or an oxide thereof, and X is one or more metals alloyed with the platinum, wherein the first region will be adjacent to the fuel inlet when the anode structure is incorporated into a fuel cell;

a second region comprising an electrocatalyst for the electrochemical oxidation of hydrogen of formula Pt-M, wherein M is a metal alloyed with the platinum and is selected from the group consisting of Ru, Rh, Ti, Cr, Mn, Fe, Co, Ni, Cu, V, Ga, Zr and Hf, wherein the second region will be adjacent to the fuel outlet when the anode structure is incorporated into a fuel cell;

wherein the first region is better at promoting the electrochemical oxidation of carbon monoxide than the second region.

2. An anode structure according to claim 1, wherein the first region covers between 5-50% of the surface area of the anode structure, and the second region covers the remainder of the surface area.

3. An anode structure according to claim 1 or claim 2, wherein Y is selected from the group consisting of Sn, Ti, V, Ta, Mo, W or an oxide thereof.

4. An anode structure according to any preceding claim, wherein X is one or more metals selected from the group consisting of Ru, Rh, Ti, Cr, Mn, Fe, Co, Ni, Cu, V, Ga, Zr and Hf.

5. An anode structure according to any preceding claim, wherein the first region comprises a Pt-Mo electrocatalyst.

6. An anode structure according to any preceding claim, wherein the first region further comprises an electrocatalyst for the electrochemical oxidation of hydrogen.

7. An anode structure according to claim 6, wherein the electrocatalyst for the electrochemical oxidation of hydrogen is of formula Pt-M, wherein M is a metal alloyed with the platinum and is selected from the group consisting of Ru, Rh, Ti, Cr, Mn, Fe, Co, Ni, Cu, V, Ga, Zr and Hf.

8. An anode structure according to any preceding claim, wherein the first region comprises only one electrocatalyst, and the electrocatalyst is of formula Pt-Y or Pt-Y-X, wherein Y is a bronze-forming element or Sn, or an oxide thereof and X is one or more metals alloyed with the platinum, and the second region comprises only one electrocatalyst, and the electrocatalyst is of formula Pt-M, wherein M is a metal alloyed with the platinum and is selected from the group consisting of Ru, Rh, Ti, Cr, Mn, Fe, Co, Ni, Cu, V, Ga, Zr and Hf.

9. An anode structure according to claim 8, wherein the first region comprises only one electrocatalyst, and the electrocatalyst is Pt-Mo, and the second region comprises only one electrocatalyst, and the electrocatalyst is Pt-Ru.

10. A membrane electrode assembly comprising an anode structure according to any preceding claim.

11. A fuel cell having a fuel inlet and a fuel outlet, wherein the fuel cell comprises an anode structure and the anode structure comprises

a first region comprising an electrocatalyst of formula Pt-Y or Pt-Y-X, wherein Y is a bronze-forming element or Sn, or an oxide thereof, and X is one or more metals alloyed with the platinum, wherein the first region is adjacent to the fuel inlet,

a second region comprising an electrocatalyst for the electrochemical oxidation of hydrogen of formula Pt-M, wherein M is a metal alloyed with the platinum and is selected from the group consisting of Ru, Rh, Ti, Cr, Mn, Fe, Co, Ni, Cu, V, Ga, Zr and Hf, wherein the second region is adjacent to the fuel outlet,

wherein the first region is better at promoting the electrochemical oxidation of carbon monoxide than the second region.

12. A method of using a fuel cell according to claim 11, wherein reformat gas is supplied to the fuel cell.

Patentansprüche

1. Anodenstruktur zur Einfügung in eine Brennstoffzelle, die einen Brennstoffeinlass und einen Brennstoffauslass umfasst, wobei die Anodenstruktur Folgendes umfasst:

eine erste Region, die einen Elektrokatalysator mit der Formel Pt-Y oder Pt-Y-X umfasst, wobei Y ein Bronze bildendes Element oder Sn oder ein Oxid davon ist und X ein oder mehrere mit Platin legierte Metalle ist, wobei die erste Region neben dem Brennstoffeinlass angeordnet sein wird, wenn die Anodenstruktur in eine Brennstoffzelle eingefügt ist;

eine zweite Region, die einen Elektrokatalysator zur elektrochemischen Oxidation von Wasserstoff mit der Formel Pt-M umfasst, wobei M ein mit Platin legiertes Metall ist, und aus der Gruppe bestehend aus Ru, Rh, Ti, Cr, Mn, Fe, Co, Ni, Cu, V, Ga, Zr und Hf ausgewählt ist, wobei die zweite Region neben dem Brennstoffauslass angeordnet sein wird, wenn die Anodenstruktur in eine Brennstoffzelle eingefügt ist;

wobei die erste Region hinsichtlich der Förderung der elektrochemischen Oxidation von Kohlenmonoxid besser als die zweite Region ist.

2. Anodenstruktur nach Anspruch 1, wobei die erste Region zwischen 5 - 50 % der Oberfläche der Anodenstruktur abdeckt und die zweite Region den Rest der Oberfläche abdeckt.

3. Anodenstruktur nach Anspruch 1 oder 2, wobei Y aus der Gruppe bestehend aus Sn, Ti, V, Ta, Mo, W oder einem Oxid davon ausgewählt ist.

4. Anodenstruktur nach einem der vorhergehenden Ansprüche, wobei X ein oder mehrere Metalle ist, das bzw. die aus der Gruppe bestehend aus Ru, Rh, Ti, Cr, Mn, Fe, Co, Ni, Cu, V, Ga, Zr und Hf ausgewählt ist bzw. sind.

5. Anodenstruktur nach einem der vorhergehenden Ansprüche, wobei die erste Region einen Pt-Mo-Elektrokatalysator umfasst.

6. Anodenstruktur nach einem der vorhergehenden Ansprüche, wobei die erste Region weiterhin einen Elektrokatalysator zur elektrochemischen Oxidation von Wasserstoff umfasst.

7. Anodenstruktur nach Anspruch 6, wobei der Elektrokatalysator zur elektrochemischen Oxidation von Wasserstoff die Formel Pt-M aufweist, wobei M ein Metall ist, das mit dem Platin legiert ist, und aus der Gruppe bestehend aus Ru, Rh, Ti, Cr, Mn, Fe, Co, Ni, Cu, V, Ga, Zr und Hf ausgewählt ist.

8. Anodenstruktur nach einem der vorhergehenden Ansprüche, wobei die erste Region nur einen Elektrokatalysator umfasst und der Elektrokatalysator die Formel Pt-Y oder Pt-Y-X aufweist, wobei Y ein Bronze bildendes Element oder Sn oder ein Oxid davon ist und X ein oder mehrere mit Platin legierte Metalle ist, und die zweite Region nur einen Elektrokatalysator umfasst und der Elektrokatalysator die Formel Pt-M aufweist, wobei M ein mit Platin legiertes Metall ist, und aus der Gruppe bestehend aus Ru, Rh, Ti, Cr, Mn, Fe, Co, Ni, Cu, V, Ga, Zr und Hf ausgewählt ist.

9. Anodenstruktur nach Anspruch 8, wobei die erste Region nur einen Elektrokatalysator umfasst und der Elektrokatalysator Pt-Mo ist, und die zweite Region nur einen Elektrokatalysator umfasst und der Elektrokatalysator Pt-Ru ist.

10. Membranelektrodeneinheit, die eine Anodenstruktur nach einem der vorhergehenden Ansprüche umfasst.

11. Brennstoffzelle mit einem Brennstoffeinlass und einem Brennstoffauslass, wobei die Brennstoffzelle eine Anodenstruktur umfasst und die Anodenstruktur Folgendes umfasst:

eine erste Region, die einen Elektrokatalysator mit der Formel Pt-Y oder Pt-Y-X umfasst, wobei Y ein Bronze bildendes Element oder Sn oder ein Oxid davon ist und X ein oder mehrere mit Platin legierte Metalle ist, wobei die erste Region neben dem Brennstoffeinlass angeordnet ist,

eine zweite Region, die einen Elektrokatalysator zur elektrochemischen Oxidation von Wasserstoff mit der Formel Pt-M umfasst, wobei M ein mit Platin legiertes Metall ist, und aus der Gruppe bestehend aus Ru, Rh, Ti, Cr, Mn, Fe, Co, Ni, Cu, V, Ga, Zr und Hf ausgewählt ist, wobei die zweite Region neben dem Brennstoffauslass angeordnet ist,

wobei die erste Region hinsichtlich der Förderung der elektrochemischen Oxidation von Kohlenmonoxid besser als die zweite Region ist.

- 5 12. Verfahren zur Verwendung einer Brennstoffzelle nach Anspruch 11, wobei der Brennstoffzelle Reformatgas zugeführt wird.

Revendications

- 10 1. Structure d'anode destinée à une incorporation dans une pile à combustible comprenant une admission de combustible et une évacuation de combustible, où la structure d'anode comprend :
- 15 - une première région comprenant un électrocatalyseur de formule Pt-Y ou Pt-Y-X, où Y représente un élément formant du bronze ou Sn ou un oxyde de ceux-ci et X représente un ou plusieurs métaux alliés avec le platine, où la première région sera adjacente à l'admission de combustible lorsque la structure d'anode est incorporée dans une pile à combustible ;
 - une deuxième région comprenant un électrocatalyseur pour l'oxydation électrochimique d'hydrogène de formule Pt-M, où M représente un métal allié avec le platine et est choisi dans le groupe constitué par Ru, Rh, Ti, Cr, Mn, Fe, Co, Ni, Cu, V, Ga, Zr et Hf, où la deuxième région sera adjacente à l'évacuation du combustible lorsque la structure d'anode est incorporée dans une pile à combustible ;
 - 20 - où la première région est un meilleur promoteur de l'oxydation électrochimique du monoxyde de carbone que la deuxième région.
- 25 2. Structure d'anode selon la revendication 1, où la première région couvre entre 5-50% de la surface superficielle de la structure d'anode et la deuxième région couvre le reste de la surface superficielle.
3. Structure d'anode selon la revendication 1 ou la revendication 2, où Y est choisi dans le groupe constitué par Sn, Ti, V, Ta, Mo, W ou un oxyde de ceux-ci.
- 30 4. Structure d'anode selon l'une quelconque des revendications précédentes, où X représente un ou plusieurs métaux choisis dans le groupe constitué par Ru, Rh, Ti, Cr, Mn, Fe, Co, Ni, Cu, V, Ga, Zr et Hf.
5. Structure d'anode selon l'une quelconque des revendications précédentes, où la première région comprend un électrocatalyseur Pt-Mo.
- 35 6. Structure d'anode selon l'une quelconque des revendications précédentes, où la première région comprend en outre un électrocatalyseur pour l'oxydation électrochimique d'hydrogène.
- 40 7. Structure d'anode selon la revendication 6, où l'électrocatalyseur pour l'oxydation électrochimique d'hydrogène présente la formule Pt-M, où M représente un métal allié avec le platine et est choisi dans le groupe constitué par Ru, Rh, Ti, Cr, Mn, Fe, Co, Ni, Cu, V, Ga, Zr et Hf.
- 45 8. Structure d'anode selon l'une quelconque des revendications précédentes, où la première région ne comprend qu'un électrocatalyseur et l'électrocatalyseur présente la formule Pt-Y ou Pt-Y-X, où Y représente un élément formant du bronze ou Sn, ou un oxyde de ceux-ci et X représente un ou plusieurs métaux alliés avec le platine et la deuxième région ne comprend qu'un électrocatalyseur et l'électrocatalyseur présente la formule Pt-M, où M est un métal allié avec le platine et est choisi dans le groupe constitué par Ru, Rh, Ti, Cr, Mn, Fe, Co, Ni, Cu, V, Ga, Zr et Hf.
- 50 9. Structure d'anode selon la revendication 8, où la première région ne comprend qu'un électrocatalyseur et l'électrocatalyseur est Pt-Mo et la deuxième région ne comprend qu'un électrocatalyseur et l'électrocatalyseur est Pt-Ru.
10. Assemblage d'électrode à membrane comprenant une structure d'anode selon l'une quelconque des revendications précédentes.
- 55 11. Pile à combustible comprenant une admission de combustible et une évacuation de combustible, où la pile à combustible comprend une structure d'anode et la structure d'anode comprend
- une première région comprenant un électrocatalyseur de formule Pt-Y ou Pt-Y-X, où Y représente un élément

EP 1 749 322 B1

formant du bronze ou Sn ou un oxyde de ceux-ci et X représente un ou plusieurs métaux alliés avec le platine, où la première région est adjacente à l'admission de combustible,

- une deuxième région comprenant un électrocatalyseur pour l'oxydation électrochimique d'hydrogène de formule Pt-M, où M représente un métal allié avec le platine et est choisi dans le groupe constitué par Ru, Rh, Ti,

5 Cr, Mn, Fe, Co, Ni, Cu, V, Ga, Zr et Hf, où la deuxième région est adjacente à l'évacuation du combustible,

- où la première région est un meilleur promoteur de l'oxydation électrochimique du monoxyde de carbone que la deuxième région.

10 **12.** Procédé d'utilisation d'une pile à combustible selon la revendication 11, où du gaz obtenu par reformage est alimenté dans la pile à combustible.

15

20

25

30

35

40

45

50

55

Fig. 1

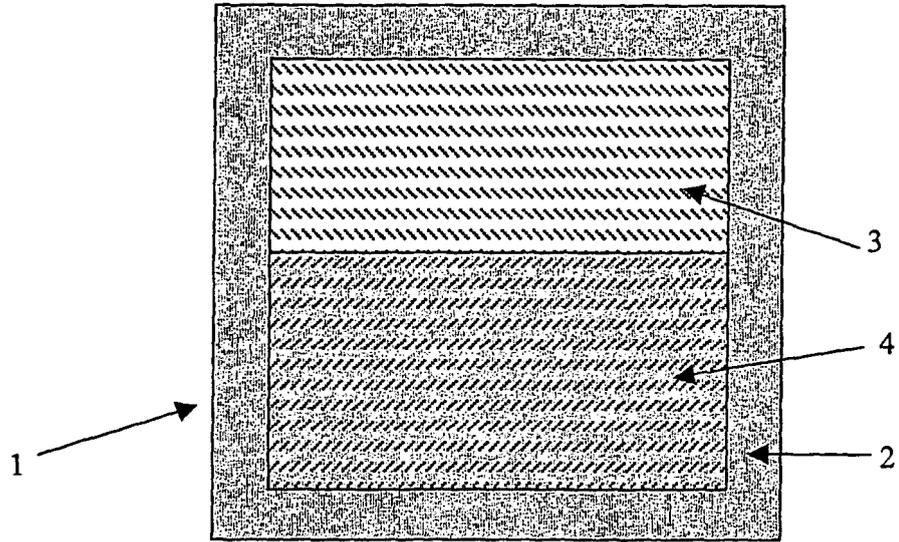


Fig. 2

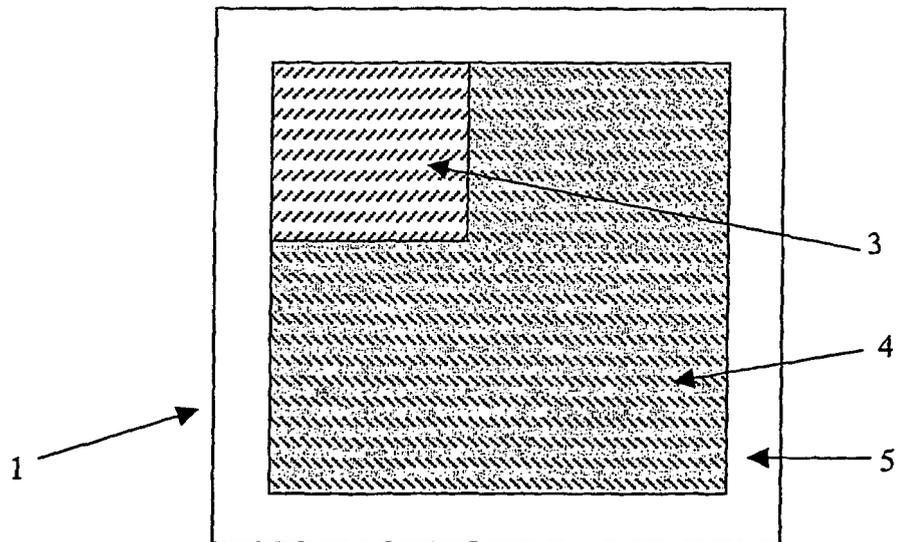
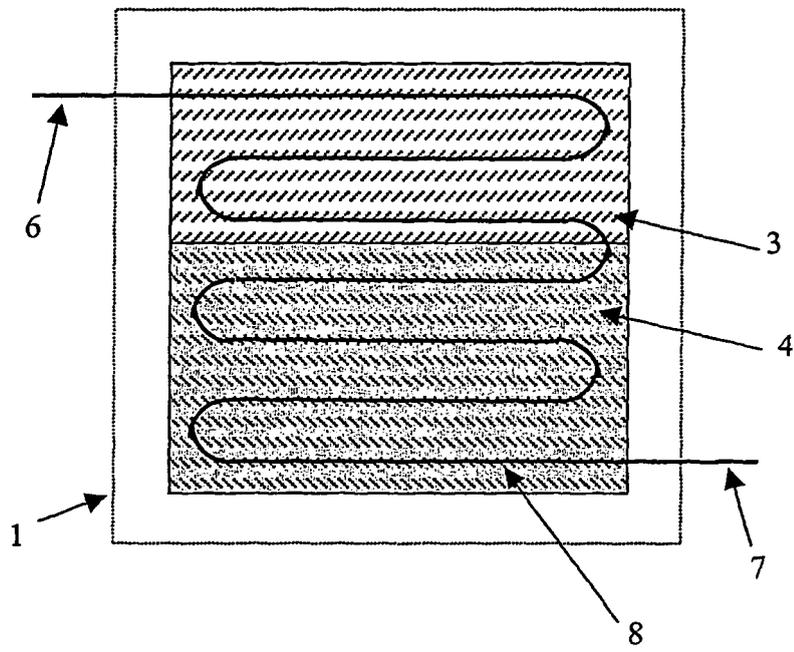


Fig. 3



REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- WO 0035037 A [0007] [0026] [0040]
- WO 2004091004 A [0008]
- US 5871860 A [0009]
- EP 0736921 A [0010]
- WO 02091504 A [0011]
- EP 0899805 A [0012]
- EP 0838872 A [0013]
- EP 875524 A [0028]
- EP 731520 A [0029] [0040]

Non-patent literature cited in the description

- *Electrochimica Acta*, vol. 43 (24), 3637-3644 [0014]
- *J. Phys. Chem. B*, vol. 101 (20), 3910-3913 [0015]